



Underground Storage Tanks Fact Sheet

Analytical Methodologies for Fuel Oxygenates

What is the purpose of this fact sheet?

This fact sheet provides information for state and federal regulators, laboratory analysts, consultants, and contractors about EPA's validated analytical methods for common fuel oxygenates.

What are fuel oxygenates?

Fuel oxygenates are primarily ethers and alcohols specifically added to gasoline to increase the octane content, promote cleaner burning in gasoline engines, and/or improve other performance characteristics. The most common fuel oxygenates are methyl tertiary-butyl ether (MTBE) and ethanol. Other fuel oxygenates include: tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), diisopropyl ether (DIPE), tertiary-amyl ethyl ether (TAE), tertiary-butyl alcohol (TBA), tertiary-amyl alcohol (TAA), and methanol.

How widespread is fuel oxygenate contamination?

Fuel oxygenates may be present at any underground storage tank (UST) site because different combinations of oxygenates in varying concentrations have been used in gasoline for more than 30 years. Oxygenates may also occur as unintentional components of other fuels (for example diesel fuel, jet fuel, and heating oil).

What methods are available to analyze for oxygenates?

Analytical methods for petroleum hydrocarbons (usually benzene, toluene, ethylbenzene, and the isomers of xylene, or collectively "BTEX") are well established and some of these protocols have been "modified" to include oxygenates as individual target compounds. Until recently, however, validated EPA analytical methods existed for only a few of the oxygenates that may be present in fuel (specifically ethanol, methanol, and TBA).

What potential problems may occur if hydrocarbon methods are used for oxygenate analysis?

Methods which were developed for analysis of petroleum hydrocarbons in water samples may or may not be appropriate for fuel oxygenates. Potential problems associated with non-validated methods include:

1. **Analytical instruments are not routinely calibrated for oxygenates** - Conventional analytical procedures designed for petroleum hydrocarbons have the capability to detect MTBE and the other ethers, but they are rarely calibrated for the fuel oxygenate ethers (other than MTBE).
2. **Inappropriate methods may be used for sample analysis** - Method 8021 (GC/PID) cannot be regarded as a consistently reliable analytical tool for the analysis of oxygenates because it is unable to detect alcohols and most ethers and it may yield either false positives or false negatives for MTBE. These problems are primarily due to coelution interferences and to the high ionization energies of many oxygenates. Method 8015 (GC/FID) can detect oxygenates at low concentrations, but it cannot provide positive confirmation of the chemical identity of the analyte that is detected. Therefore, compounds that coelute may be mistaken for one another leading to over- or under-reporting of actual concentrations of the oxygenate compounds.
3. **Detection limits (particularly for alcohols) may be higher than regulatory standards** - Because alcohols are so highly soluble in water, extracting them for analysis is difficult and reporting limits are generally much higher than those for BTEX and MTBE. In order to consistently achieve low detection levels for TBA (and other alcohols), sample preparation procedures must be modified to increase method sensitivity.
4. **Hydrolysis of ethers and formation of alcohols** - Acid-catalyzed hydrolysis (breakdown) of ethers may occur during analysis, particularly if the samples are heated to improve the extraction efficiency for alcohols. This can lead to underreporting of the ether (for example MTBE) concentration and overreporting of the concentration of the corresponding alcohol (which is TBA if the ether is MTBE).

What steps may be taken to address potential analytical problems with oxygenate analysis?

1. **Routinely calibrate analytical methods for the suite of common fuel oxygenates** - Calibration of analytical instruments for the suite of common fuel oxygenates can be adopted as part of the laboratory's standard operating procedures. Even when using EPA methods, EPA encourages flexibility in selecting target analyte lists that are tailored to site-specific conditions.

2. **Use appropriate methods for sample analysis** - For example, determinative methods evaluated in EPA's study that are capable of identifying fuel oxygenates at 5 µg/L or lower in fuel-contaminated groundwater samples include Method 8260 (GC/MS) and Method 8015 (GC/FID). However, Method 8260 confirms the chemical identity of the analyte detected while Method 8015 does not.

3. **Modify sample preparation methods to increase sensitivity and decrease detection limits** - To increase the sensitivity of the method and lower the method detection limit, samples can be heated during the preparative phase. Heating is particularly important for preparing samples to be analyzed for alcohols, however, samples to be analyzed for ethers may be prepared at room temperature. EPA recently completed a method evaluation study which found that for Method 5030 (purge-and-trap) and Method 5021 (static headspace), heating samples to 80°C for 30 minutes could consistently result in a detection limit of 5 µg/L or lower for MTBE, TBA, ETBE, TAME, TAEE, TAA, DIPE, and acetone. Note, however, that heating acidified samples will hydrolyze ether to alcohol and, therefore, the chemical preservation method must be changed as described in #4 below.

4. **Change the chemical preservation method to avoid the potential for ether hydrolysis** - Groundwater samples to be analyzed for hydrocarbons in addition to fuel oxygenates must be preserved using both a chemical preservative and refrigeration (preferably to 4° C) and also analyzed within prescribed holding times (generally 14 days or less). Acid is the most commonly used chemical preservative as it is effective in preventing biodegradation in the sample when the pH is less than 2. Acid may be used to preserve groundwater samples to be analyzed for ethers (and BTEX) if the preparation is conducted at room temperature. However, when acidified samples are heated to 80° C (which is necessary if alcohols are the target analytes) during the preparative phase (as with Methods 5030 or 5021), ethers present in the sample will hydrolyze. An alternative to chemical preservation with acid, and consequent avoidance of ether hydrolysis, is base preservation to raise the pH to greater than 11. The high pH is as effective in preventing the biodegradation of organic compounds in the sample as is a low pH, but the elevated pH has no adverse chemical effect on hydrocarbons or fuel oxygenates. Trisodium phosphate dodecahydrate ("TSP") has been determined to be effective and safe for this purpose. TSP may also be used to neutralize acid-preserved samples prior to analysis, if an elevated temperature sample preparative method is to be used.

Where can I get additional information?

For additional information about analytical methods, call EPA's Methods Information Communication Exchange (MICE) hotline at 703-676-4690, or visit the MICE web site at <http://www.epa.gov/SW-846/mice.htm>. For information about the underground storage tank program, visit <http://www.epa.gov/oust>. More details on the issues discussed in this fact sheet and EPA's analytical methods study are available in the October 2002 issue of *LUSTLine* (Bulletin #42). The article, "Analytical Methods for Fuel Oxygenates", is accessible on the internet at <http://www.epa.gov/oust/mtbe/LL42Analytical.pdf>.